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(12) **APPLICATION FOR PATENT OF INVENTION A1**

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(54) DENTIFRICE WITH A GOOD RATIO OF CLEANING POWER/ABRASIVE POWER

(57) The present invention concerns a weakly abrasive dentifrice, characterized in that it contains as abrasive cleaning agent a mixture of abrasive mineral agents with particle sizes of less 20 μm and an abrasive power less than 50, as well as a natural or synthetic organic polymer that is insoluble in water, which does not gel and which has particle sizes comprised between 50 and 100 μm.

The present invention concerns a dentifrice with a good ratio of cleaning power to abrasive power.

In a general manner, the formula of a dentifrice comprises a solid phase and a liquid phase. The solid phase is made up of abrasive cleaning agents kept in suspension in the liquid phase. This liquid phase comprises a carrier such as glycerin, sorbitol, or propylene glycol and water. Principally, one or more gelling agents and essential oils that may be made into emulsions, and, possibly, agents with specific activity can be added to this base.

When the dentifrice is used for cleaning teeth, experience and previous usage have shown the necessity of incorporating a powder in the formulation. Current technique applies this principle by using numerous finely powdered products in order to complement the mechanical action of the brush.

Numerous synthetic or natural substances have been tested for this usage; for example, dicalcium or tricalcium phosphate, sodium metaphosphate, calcium carbonate, calcium pyrophosphate, alumina, silicon oxide, silica, hydrated silicates, and kaolin can be cited.

The action of these abrasives during brushing is to break up bacterial dental plaque that must be eliminated daily in order to prevent it from building up on the teeth and to prevent its mineralization to form tartar. The abrasives also permit eliminating exogenous discolorations (fine films of organic material originating from saliva).

It is known that these powders can have variable actions on enamel and dentin, particularly on their hardness.

While the action of these powders is beneficial for the elimination of dental plaque, their effects on the teeth are harmful due to damage to the enamel and especially the more delicate dentin which appears when gums retreat.

It is the cleaning power, i.e. the ability to eliminate dental plaque and stains, which characterizes the efficacy of a dentifrice, without it necessarily being endowed with a strong abrasive power.

Classical dentifrice studies essentially refer to the abrasive power of the paste. However, it appears desirable to optimize these two properties. A good index for evaluating the results of this optimization of the cleaning and abrasive properties is the ratio: cleaning power/abrasive power (CP/AP). According to this criterion, it is therefore clear that the object of the invention is the choice of a mixture having the highest cleaning power possible with the weakest abrasive power, or a high CP/AP ratio.

During its research, the Applicant was able to show that it is impossible to obtain useful values by using a single abrasive cleaning agent.

More particularly, the present invention concerns a weakly abrasive dentifrice, characterized in that it comprises as the abrasive cleaning agent a mixture of mineral abrasive agents, having particle sizes of less than 20 μm as well as a natural or synthetic organic polymer which is insoluble in water but hydrophilic. This mixture permits obtaining an abrasive power of less than 70 and greater than 20, according to the knowledge of the Applicant, and a high cleaning action over large dental surfaces, due to the large particles it contains,

as well as an effective action in the spaces between the teeth due to its small particles.

Particles of hydrated polymer are included as a solid diluent and this separates the mineral particles and reduces their abrasive effect by coating them with a hydrophilic matrix.

The particle sizes of the polymers are comprised between 50 and 100 μm.

Of course, this dentifrice will also contain other components known in the dentifrice field, in particular humectants, gelling agents and foaming agents.

In order to obtain an abrasive power of less than 50, it is often necessary to resort to a mixture of mineral abrasives of small particle size, one of which has a weak abrasiveness and the other with an average abrasiveness.

Thus, the present invention proposes a dentifrice with an optimum cleaning power/abrasive power ratio, characterized in that it comprises, for example

- 10% to 60% by weight of humectant,
- 0.1% to 40% by weight of gelling agent,
- 0.1 to 2% by weight of detergent,
- 5 to 75% by weight of abrasive cleaning agent comprising:
  - a mineral abrasive of small particle size and average abrasiveness;
  - a mineral abrasive of small particle size and weak abrasiveness;
  - a polymer whose particles are comprised between 50 and 100 μm.

As mineral abrasive of small particle size and weak abrasiveness, a mineral powder of particle size comprised between 5 and 10 μm and an

abrasiveness of less than 30, preferably less than 10, can be used according to the invention.

For example, an amorphous silica can be used, although any other mineral powder having these characteristics of particle size and abrasiveness can be considered.

One example of such an abrasive is SYLO 82® from Grace.

As an abrasive mineral of small particle size and average abrasiveness, a mineral powder of particle size of less of than 20 μm and greater than 5 μm, and with an abrasiveness of less than 75, can be used according to the invention.

For example, a silica known under the name of SIDENT 12® can be used.

As a natural or synthetic organic polymer insoluble in water, hydrophilic polymers are preferably used, notably cellulose or its derivatives. It is very important to note that although these polymers are hydrophilic, they do not gel. This clearly differentiates them from celluloses usually used to thicken dentifrice pastes.

These powdered polymers, which have a particle size comprised between 50 and 100 μm, are known. For example, the product called AVICEL PH 105® can be used.

Judicious combinations of these three compounds, the two mineral powders of small particle size, which are weakly abrasive and of average abrasiveness, respectively, and the organic powder of large particle size based on polymers insoluble in water, permit creating a broad range of abrasiveness and cleaning power.

As polymers conforming to the criteria of the invention, the following are cited by way of nonlimiting example:

- starches, vegetable charcoal, rilsan, powders of plant cuticle or straw (rice, wheat, coffee, etc.); powders of fruit or nut husks: walnuts, hazelnuts, almonds, etc., of various origins, powders of fruit pits, etc.

Table I below collects the measurements of abrasive power and cleaning power of different dentifrice pastes in which the abrasive cleaning agent represents in total 18% of the composition by weight and has the composition indicated in the first three columns. The last column of the table gives the value of the cleaning power/abrasive power ratio.

TABLE I

AVICEL PH 105	SIDENT 12	SYLOBLANC 82	ABRASIVE POWER*	CLEANING POWER*	CP/AP
18	0	0	0.0390±0.004	692±8	17743
0	18	0	0.0576±0.006	648±8	11250
0	0	18	0.0430±0.002	698±8	16232
9	9	0	0.0464±0.002	672±11	14483
9	0	9	0.0452±0.003	708±8	15664
0	9	9	0.0523±0.005	686±15	13116
6	6	6	0.0456±0.0015	702±18	15395

*REFLECTOMETRIC MEASUREMENT

The abrasive and cleaning powers were respectively measured experimentally according to the protocols presented in Examples 1 and 2.

Example 3 shows the results of comparative tests for known dentifrices and for dentifrices according to the invention; the tests are conducted by the methods described in Examples 1 and 2.

By way of example, with regard to the abrasive cleaning agent in the compositions of dentifrices according to the invention, the following formula can be used:

SYLOBLANC 82®: 69%

SIDENT 12®: 9%

AVICEL PH 105®: 22%

These percentages are calculated by weight.

EXAMPLE 1:

ABRASIVE POWER

The tests were conducted on a synthetic material, plexiglas, considered by numerous authors as a good model for the behavior of dental enamel.

*Electric toothbrush machine (Patent Application No. 83 19585)

The device used is an alternating machine permitting the load applied to the toothbrush and the brushing frequency to be varied.

This machine uses the general principle for electric toothbrushes: an electric motor created by means of a push-rod, and a translation movement which drives the brushes.

It is composed of the following elements :

- a triphasic electric motor of 0.25 KW,

- a switch which controls this motor,

- a variable transmission permitting choosing the rotation frequency,

- a push-rod converting the rotation into translation,

- a carriage driven by the push-rod, which supports two rows of five vertical ball-bearing runners; in these runners slide the brush-holders that can receive the weights (150 or 200 g); they thus transmit a virtually constant and uniformly distributed vertical force to the brush bristles,

- a frame holding two ball-bearing runners on which the carriage slides,

- a meter controlled by the carriage which displays the number of back-and-forth cycles of the brushes,

- two removable containers, each permitting holding five brushes simultaneously,

- a fixed table which supports all these elements and assures stability,

- a pump which, by aspiration and backflow, assures stirring of the solutions in the containers.

*Test protocol

Sample

Plexiglas is used. The flat samples measure 130 x 30 mm^2.

Brushes

Five toothbrushes are necessary for each test. "Spirogyl" trademark brushes are used.

The tests are conducted with brushes having 32 tufts of bristles. It is therefore suitable to first pull off or cut the surplus tufts. Then two holes with a diameter of 3.2 mm spaced 28 mm apart are pierced through the bristles, after

which the handle of the toothbrush is cut. Then the brush heads are attached to the brush-holders on the electric toothbrush machine by means of two screws.

Products

The dilutions are different depending on the nature of the product and the power to be measured. If it is:

- a paste or gel dentifrice, the product dilution is ½ product by weight and ½ distilled water by weight,
- a powder, the dilution is 1/6 product by weight and 5/6 distilled water by weight.

In all cases, one should try to have a sufficient quantity to totally cover the sample, i.e. approximately 120 g.

Test

The container containing the flat sample and the product to be tested is attached under the five brushes. The brushes are then lowered into the sample and the desired load is applied to them.

The test conditions are different depending on the abrasive power. Only the speed remains constant at approximately 200 rpm.

Maximum duration of the test: 4,000 cycles

Vertical load: 170 g

The axis of the brushes is parallel to the direction of movement; the sample is rinsed with water and wiped.

The five brushes simultaneously brush the sample inside the same solution. The solution is stirred by a pump throughout the test.

Measurements

Each result is the average of 15 measurements (three measurements for each of the five brush impressions).

The result is given in the form of a mean and a standard deviation.

Reflectometry

Reflectometry is an optical method permitting measuring the reflection coefficient R of a surface

$$R = \frac{\phi_R}{\phi_i}$$

(ϕ_R reflected flux, ϕ_i incident flux).

The coefficient R is greater the closer the angle of incidence is to 90° (grazing incidence) and the better the studied surface is polished, in the case where the angle of measurement is equal to the angle of incidence.

TECHNIQUE

The method used consists of measuring the variation of the coefficient R between the intact surface of the material tested and the abraded part (see Material Chemistry 13 (1985) 503 -516).

The angle of incidence is: 45°.

The measurement angle chosen is 0°.

Under these conditions, the good correlation of the abrasive power measurements with those obtained by the RDA method is shown.

EXAMPLE 2

CLEANING POWER

The cleaning power can be evaluated by reflectometric measurement according to the STOOKEY method after staining of the enamel.

Creation of enamel inclusions

Bovine incisors or molars are sectioned in order to obtain flat enamel surfaces (10 to 20 mm^2).

These enamel samples are then placed in the bottom of plexiglas molds (the flat enamel surface is placed against the bottom of the container).

Inner dimensions of the mold: 130 x 30 mm^2

Minimal inner thickness: 3 mm

Thus 5 tooth pieces are placed in the mold.

These dimensions and this arrangement will permit adapting this type of flat sample to the electric toothbrush machine.

Once the samples are positioned in the mold, they are enclosed in a self-polymerizing resin so as to totally cover the tooth pieces.

After removing from the mold, a resin plate containing 5 enamel pieces is obtained, which enamel is then polished with finer and finer grit sandpaper: first with 180 grit, then 300 and finally 600.

In order to facilitate removing the flat samples from the mold, a strip of moistened paper is placed in the bottom of the mold to prevent the resin from sticking to the plexiglas.

Preparing the samples to receive the staining film

The enamel samples are lightly sanded to increase the adherence and accumulation of the staining material.

This procedure consists of an immersion of

-60 seconds in 0.12 N HCl,

- then: 30 s in a saturated solution of sodium carbonate,

- finally: 60 s in 1% phytic acid.

The samples are then rinsed and fixed to the rotating device.

Deposit of artificial dental plaque

Two plexiglas disks with grooves made in them are positioned parallelly, with a bronze shaft passing through their center.

A motor rotating at the speed of 2 rpm turns the shaft and engages the wheel. The enamel samples are immersed alternatingly in the staining medium and in air.

The staining medium

Proportions:

2.7 g instant coffee

2.7 g instant tea

2.0 g gastric mucus

800 ml of sterilized soy trypto-casein medium

26 ml of a 24 h culture of micrococcus luteus (= sarcina lutea)

The assembly of wheel, flat samples and staining medium is then placed in a thermostated chamber (37°C) with the samples rotating alternatingly through the bath and air. The staining medium is replaced twice a day for four consecutive days.

During each medium change, the samples are rinsed with distilled water to remove loose deposits.

After four days, a dark staining film appears on the enamel surfaces.

Four days later the samples are removed from the device, rinsed well, air-dried for 10 minutes and refrigerated until they are used.

The dental flat sample is made up again and the tests can be conducted.

Tests of dentifrice pastes by the STOOKEY method

Necessary equipment:

- pastes to be tested
- electric toothbrush machine (see characteristics in the "Abrasive Power" section, Example 1),
- PHOTODYNE Model 99 XL densitometer reflectometer

A preliminary visual evaluation of the intensity of the artificial dental flat sample is conducted before brushing. After brushing of the enamel surfaces by the material to be tested, a second evaluation of this intensity will permit us to deduce the quantity of stain removed, and therefore the cleaning power of the dentifrice.

The evaluations were performed by a reproducible reflectometric measurement method.

Reflectometry

In order to eliminate the disadvantages of a subjective criterion, such as visual appearance, reflectometry measurements were developed in order for the device to evaluate the intensity of the color of the film deposited (PHOTODYNE Model 99 xl densitometer reflectometer).

A beam of light is projected by fiber optics to the level of the enamel sample. According to the color intensity of the surface struck by the beam, the beam will be absorbed to a greater or lesser degree, and the reflected beam will therefore not have the same value. A second series of fiber optics will capture this reflected beam, the latter being then converted into current intensity.

In order to prevent the reflection of the incident beam due to the polish of the stained surface, it is necessary to interpose an opaque surface (for example tracing paper) between the sample and the reading head, so as to work with constant diffusion.

All the flat samples are thus graded by means of this device.

Each sample is measured in six different places, at normal incidence. The machine is zeroed with a piece of white enamel. Therefore, an average of the amount of light reflected before brushing is obtained for each sample, measured under identical luminosity conditions.

Brushing of the samples

Five samples per dentifrice tested were used; 75 g of dentifrice were diluted in 75 ml water.

Vertical load: 170 g

Maximum duration of the test: 4,000 cycles

The brush axis has an angle of 5 to 10° with regard to the direction of movement in order to brush homogeneously.

After brushing, the samples are rinsed, dried with a hair-dryer and the quantity of staining remaining is reevaluated.

The difference between the scores before and after brushing is considered to represent the capacity of the dentifrice tested to remove dental plaque.

The cleaning power is expressed by the difference in the reflecting power before and after brushing.

EXAMPLE 3

A comparative study between a dentifrice composition conforming to the present invention and a sampling of commercial compositions was conducted.

The table below illustrates the results of the study.

The "composition according to the present invention" of Table II is a dentifrice composition in which an abrasive cleaning agent conforming to the present invention was used.

The measurements were conducted according to the protocols described above.

Regardless of the method used, the composition according to the invention appears to be a paste that cleans very well with little abrasion.

TABLE II

COMPOSITION	ABRASIVE POWER	CLEANING POWER	CLEANING POWER/ABRASIVE POWER
		X1E-04	
COMPOSITION ACCORDING TO THE INVENTION	0.0426±0.0011	718±8	16854
COMMERCIAL DENTIFRICE A	0.066±0.0015	672±17	10182
COMMERCIAL DENTIFRICE B	0.075±0.016	541±57	7213
COMMERCIAL DENTIFRICE C	0.092±0.008	663±34	7206
COMMERCIAL DENTIFRICE D	0.174±0.026	795±114	4568
COMMERCIAL DENTIFRICE E	0.134±0.016	604±34	4508
COMMERCIAL DENTIFRICE F	0.126±0.013	556±57	4413
COMMERCIAL DENTIFRICE G	0.120±0.004	462±34	3850
COMMERCIAL DENTIFRICE H	0.196±0.015	688±68	3510
COMMERCIAL DENTIFRICE I	0.241±0.075	706±102	2929
COMMERCIAL DENTIFRICE J	0.258±0.027	675±57	2616
COMMERCIAL DENTIFRICE K	0.267±0.026	695±46	2602
COMMERCIAL DENTIFRICE L	0.277±0.016	695±46	2509
COMMERCIAL DENTIFRICE M	0.269±0.043	454±91	1687

CLAIMS

1. A weakly abrasive dentifrice, characterized in that it comprises as abrasive cleaning agent a mixture of mineral abrasive agents, having particle sizes of less than 20 μm and an abrasive power of less than 50, as well as a natural or synthetic organic polymer insoluble in water, which does not gel and which has particle sizes comprised between 50 and 100 μm.

2. The dentifrice according to claim 1, further characterized in that the polymer is a hydrophilic polymer.

3. The dentifrice according to claim 2, further characterized in that the polymer is cellulose or one of its derivatives.

4. The dentifrice according to claim 3, further characterized in that cellulose or a cellulose derivative is chosen from among AVICEL®, crushed fruit pits (prune pits), starches, plant charcoals, rilsan, powders of plant cuticles or straw, powders of fruit or nut husks of various origins.

5. The dentifrice with optimum abrasive cleaning power according to one of claims 1 to 4, further characterized in that it comprises

- 10 to 60% by weight of humectant,

- 0.1 to 40% by weight of gelling agent,

- 0.1 to 2% by weight of detergent,

-5 to 75% by weight of abrasive cleaning agent,

the mineral abrasive agent mixture comprising at least:

•one mineral abrasive of small particle size and average abrasiveness,

•one mineral abrasive of small particle size and weak abrasiveness.

6. The dentifrice according to claim 5, further characterized in that it contains 10 to 30% abrasive cleaning agent.

7. The dentifrice according to one of claims 5 or 6, further characterized in that the mineral abrasive of small particle size and weak abrasiveness has a particle size of less than approximately 10 μm, preferably 5 μm, and an abrasiveness of less than 30, preferably less than 10.

8. The dentifrice according to one of claims 5 to 7, further characterized in that the mineral abrasive of small particle size and weak abrasiveness is a synthetic amorphous silica.

9. The dentifrice according to one of claims 5 to 8, further characterized in that the abrasive of small particle size and weak abrasiveness is SYLOBLANC 82®.

10. The dentifrice according to one of claims 5 to 9, further characterized in that the mineral abrasive of small particle size and average abrasiveness has a particle size of less than approximately 20 μm, and greater than 5 μm, and an abrasiveness of less than 100, preferably less than 75.

11. The dentifrice according to one of claims 1 to 10, further characterized in that the abrasive of small particle size and average abrasiveness is a silica.

12. The dentifrice according to one of claims 1 to 11, further characterized in that the abrasive of small particle size and average abrasiveness is SIDENT 12®.

13. The dentifrice according to one of claims 1 to 12, further characterized in that the organic polymer insoluble in water is AVICEL PH 105®.

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(71) Demandeur(s) : *Laboratoires PHARMASCIENCE.* — FR.

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(54) Dentifrice à bon rapport pouvoir nettoyant/ pouvoir abrasif.

(57) La présente invention concerne un dentifrice faiblement abrasif, caractérisé en ce qu'il comporte à titre d'agent abrasif nettoyant un mélange d'agents abrasifs minéraux ayant des dimensions particulaires inférieures à 20 μm et un pouvoir abrasif inférieur à 50 ainsi qu'un polymère organique naturel ou synthétique non soluble dans l'eau, ne se gélifiant pas et ayant des dimensions particulaires comprises entre 50 et 100 μm.

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